On the Variation of the Core Resonance Integral in Semi-empirical Molecular Orbital Calculations

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In a recently suggested scheme[1] for the evaluation of semi-empirical parameters appropriate to π-electron systems, the following linear relation for the core resonance integral was assumed

$$\beta = \beta^0 + \delta(R - R^0) \qquad (1)$$

where β^0 and δ are parameters to be determined empirically, and where R^0 is a chosen reference distance for the bond considered. These parameters have been evaluated for a series of different bonds by using experimental information on appropriate model systems. The sources of information applied have been molecular spectra, ionization potentials, and molecular structure data. In Table 1 the estimated β-values for four different kinds of chemical bonds, all of the type $C-X$, are presented in column two.[1-4] For the purpose of comparison all the values refer to the same internuclear distance, 1.34 Å.

The integrals have been converted by means of eqn. (1) by assuming a common δ-value for all the bonds. The value adopted is the one determined for the $C-C$ bond, 3.05 eV/Å. This assumption has been applied in all the semi-empirical studies referred to above.

As is revealed by the data in the table, the magnitude of β is decreasing by going from the bond $C-C$ to the bond $C-F$. A discussion of this variation in terms of the nature of the $2p\pi$-orbitals centered at the atoms leads to the natural conclusion that the decrease of the numerical value of the integral is directly related to the contraction of the orbital by going from C to F.

The most simple way to relate the core resonance integral to the extension of the basic orbitals in a quantitative way is to apply the formula

$$\beta = k \cdot S \qquad (2)$$

where k is a constant and where S represents the overlap integral for the bond in question.

Table 1. Numerical values of core resonance integrals estimated empirically, and calculated from overlap integrals. The integral values refer to an internuclear distance of 1.34 Å. Values in eV.

Atom X in bond C−X	Empirical β	Calculated β	Orbital exponent for atom X[a]
C	−2.59	−2.65	1.56
N	−2.25	−2.06	1.92
O	−1.80	−1.61	2.22
F	−1.30	−1.29	2.55

[a] Ref. 5.

The purpose of the present note is to investigate whether an application of the simple formula above leads to results compatible with those determined semi-empirically.

The constant k in (2) has been determined in the following way. By using the empirical methods mentioned above the integral β for the $C-C$ bond at 1.40 Å was estimated to -2.42 eV.[1] The overlap integral was evaluated at the same internuclear distance using Slater-type orbitals and the orbital exponents of Duncanson and Coulson.[5] This leads to the value -8.98 eV for the coefficient k. This constant has been assumed to be the same for all types of bonds studied here, and also to be independent of the internuclear distances.

By using this value and the appropriate overlap integral values in formula (2), the results presented in column three in the table were obtained.

As is revealed by the table the two sets of values are in fair agreement. In view of the large uncertainties in parts of the experimental material used by the empirical evaluation of the parameters, the agreement has to be considered as rather satisfactory. This also implies that the assump-

tion of a common δ-value for all bonds of the type $C-X$ in formula (1) is an acceptable procedure in the sense that it leads to β-values in accordance with those calculated by eqn. (2).

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Thiophene Analogues of Fluorene

IV. An Unusual Behaviour of a Cyclopentadithiophenone in the Reaction with Dienophiles

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W e have earlier demonstrated that 2,3,4,5-tetramethyl-7H-cyclopenta-[1,2-b:4,3-b']dithiophene-7-one (I) [1] reacts as a diene in the reaction with dimethyl acetylenedicarboxylate or maleic anhydride, the central formal cyclopentadienonic moiety of I functioning as the reacting dienic grouping.[1]

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We have now also found that I reacts similarly with phenylacetylene to yield 1,2,7,8-tetramethyl-4-phenylbenzo[1,2-b:-4,3-b']dithiophene (II) in 39 % yield. The structure is based on a correct elementary analysis and on its spectral properties. Similarly, when the other "cyclopentadienonic" fluorenone analogue, 2,3,5,6-tetramethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one (III) [2] was reacted with dimethyl acetylenedicarboxylate and phenyl acetylene, 4,5-dicarbomethoxy-2,3,6,7-tetramethylbenzo[2,1-b:3,4-b']dithiophene (IV) and 2,3,6,7-tetramethyl-4-phenylbenzo[2,1-b:3,4-b']dithiophene (V) was obtained. The structure is based on correct elementary analyses and spectral properties. The NMR spectrum of V shows four methyl resonances, one of which appears at higher field than the other three. We ascribe this signal to the methyl group in the 3-position. The shift towards higher field is probably caused by the anisotropy effect of the neighbouring phenyl group.

Recently Wynberg [3] and coworkers and Loader and Timmons [4] prepared several thiophene and furan analogues of phenanthrene by photochemically induced cyclization of thienyl ethenes. However, the synthesis of benzo[2,1-b:3,4-b']dithiophene by this method failed.[3]

The driving force for the easy decarbonylation in the reaction of I and III with acetylenes certainly is the formation of the aromatic analogues of phenantrene and similar decarbonylations have been observed with simple cyclopentadienones.[5]

However, the reaction of III with maleic anhydride and N-phenylmaleimide gave rise to unexpected products. In both cases evolution of hydrogen sulphide was noticed and the mass spectra of the isolated product showed molecular ions at 34 mass units lower than expected for the primary Diels-Alder adduct and analyzed correctly for such products. The IR spectra showed the presence of keto groups and anhydride and imide rings, respectively. Due to extremely low solubility, no NMR spectra could be obtained.

The product obtained from the reaction of III with maleic anhydride was converted into a dimethyl ester. Its NMR spectrum showed in addition to the CO_2CH_3 resonance at 6.10 τ, three methyl bands with relative intensities of 3:3:6. On this basis we suggest this diester to be 7,8-dicarbomethoxy-2,3,5,6-tetramethyl-4H-indeno[1,2-b]thiophene-4-one (VI). The